AF8360 (031 EUR

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 683 149 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
06.10.1999 Bulletin 1999/40

(51) Int. Cl.[6]: C07C 21/18, C08F 214/18

(21) Application number: 95107005.1

(22) Date of filing: 09.05.1995

(54) **New peroxide curable fluoroelastomers, particularly suitable for manufacturing O-rings**
Neue peroxidhärtbare Fluorelastomere, besonderes geeignet zur Herstellung von O-Ringen
Nouveaux élastomères fluorés adaptés en particulier à la fabrication de joints toriques

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE

(30) Priority: 18.05.1994 IT MI940998

(43) Date of publication of application:
22.11.1995 Bulletin 1995/47

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EP 0 683 149 B1

## Description

[0001] The present invention relates to new peroxide curable fluoroelastomers particularly suitable for manufacturing O-rings.

[0002] Various types of fluoroelastomers are known in the art, widely used in all those fields where superior elastic properties associated with high thermochemical stability are required. For a wide survey on such products see for instance "Ullmann's Encyclopedia of Industrial Chemistry", vol. A-11, pag. 417-429 (1988, VCH Verlagsgesellschaft).

[0003] It is also known that for manufacturing sealing elements, particularly O-rings, it is necessary to use elastomers endowed with particularly low compression set values. In fact, O-ring sealing effectiveness is as better as the article, upon compression, is able to recover initial dimensions. Since the fluoroelastomers are used in a wide temperature range, compression set values should be low not only at low temperatures, but also at high temperatures. Compression set values (measured at 200°C for 70 hours, according to ASTM Standard D395, Method B) lower than 25% are generally required. More particularly, military specifications (MIL-R-83248B) asks for O-rings having a maximum compression set value of 20% (measured at 200°C for 70 hours as well).

[0004] Fluoroelastomers which can meet such requirements are those curable ionically, which need addition of curing agents (for instance polyhydroxy compounds, such as Bisphenol AF or Bisphenol A), of suitable accelerators (for instance ammonium, phosphonium or amino-phosphonium salts), and of divalent metal oxides and/or hydroxides (for instance MgO, $Ca(OH)_2$). Elastomers of this type are described for instance in patent application EP-525,685. However, ionic curing shows some drawbacks, among which the fact that a post-curing treatment is needed, generally carried out at 200°-260°C for 12-24 hours, in order to complete curing, and to eliminate volatile by-products, so as to improve and stabilize mechanical and elastic properties. This implies a remarkable increase in processing times and costs and therefore strongly limits the possibilities of large scale production.

[0005] As described in US Patent 4,243,770, fluoroelastomers can be crosslinked also by means of peroxides. To such purpose it is necessary to carry out the polymerization in the presence of suitable iodinated chain transfer agents, which introduce into the macromolecules iodine atoms in terminal position: in the presence of radicals deriving from a peroxide said iodine atoms act as cure sites in consequence of homolitic breakage of the C-I bonds. Fluoroelastomers of this type generally do not require long post-curing treatments: in some cases it is sufficient a post-curing in air at about 200°-230°C for 1-4 hours. However, such products do not meet the specifications indicated above for O-ring manufacturing: the compression set value is indeed usually high, at least equal to 28-30% or higher.

[0006] US patent 5,231,154 discloses new diiodides chain transfer agents for fluoroelastomers, giving iodine end groups on both the polymer chain which is terminated and the polymer chain which is initiated, providing fluoroelastomers having improved thermal and chemical resistances, but no improvement of mechanical properties, particularly of compression set.

[0007] The Applicant has now found a new class of fluoroelastomers as defined hereinunder, which, upon peroxide curing, need extremely short post-curing treatments (around 30-60 minutes at 180°-230°C) and are characterized by compression set values lower than 25% (measured on O-rings at 200°C for 70 hours according to ASTM Standard D395 Method B).

[0008] Therefore, a first object of the present invention are peroxide curable fluoroelastomers, having iodine atoms in terminal position, and monomeric units in the chain deriving from an iodinated olefin of formula:

$$CHR{=}CH\text{-}Z\text{-}CH_2CHR\text{-}I \tag{I}$$

wherein: R is -H or $-CH_3$; Z is a $C_1$-$C_{18}$ (per)fluoroalkylene radical, linear or branched, optionally containing one or more ether oxygen atoms, or a (per)fluoropolyoxyalkylene radical.

[0009] Further objects of the present invention are the iodinated olefins of formula (I), and the preparation process thereof, as described hereinunder.

[0010] As regards formula (I), Z is preferably a $C_4$-$C_{12}$ perfluoroalkylene radical, or a (per)fluoropolyoxyalkylene radical of formula:

$$-(Q)_p\text{-}CF_2O\text{-}(CF_2CF_2O)_m(CF_2O)_n\text{-}CF_2\text{-}(Q)_p\text{-} \tag{II}$$

wherein: Q is a $C_1$-$C_6$, preferably $C_1$-$C_3$, alkylene or oxyalkylene radical; p is 0 or 1; m and n are numbers such that the m/n ratio is from 0.2 to 5 and the molecular weight of said (per)fluoropolyoxyalkylene radical is from 400 to 10,000, preferably from 500 to 1,000. Preferably, Q is selected from: $-CH_2O-$; $-CH_2OCH_2-$; $-CH_2-$; $-CH_2CH_2-$.

[0011] The olefins of formula (I) can be prepared starting from compounds of formula I-Z-I according to the following process:

(1) adding ethylene or propylene to a compound of formula I-Z-I, thus obtaining a diiodinated product of formula:

$$I\text{-}CHR\text{-}CH_2\text{-}Z\text{-}CH_2\text{-}CHR\text{-}I \qquad (III)$$

where R and Z are defined as above;

(2) partially dehydroiodinating the product of formula (III) with a base (for instance NaOH, KOH, tertiary amines, etc.), so as to obtain the iodinated olefin of formula (I).

[0012] As to step (1), the addition of ethylene or propylene is usually carried out in the presence of suitable catalysts, such as redox systems, for instance CuI or $FeCl_3$, in solution in an organic solvent, for instance acetonitrile. The addition reaction between a perfluoroalkyliodide and an olefin is described, for instance, by M. Hudliky in "Chemistry of Organic Fluorine Compounds" (2nd Edition, Ellis Horwood Ltd., Chichester, 1976), and by R. E. Banks in "Organofluorine Chemicals and Their Industrial Applications" (Ellis Horwood Ltd, Chichester, 1979), or in J. Fluorine Chemistry, 49 (1990), 1-20 and in J. Fluorine Chemistry, 58 (1992), 1-8.

[0013] The dehydroiodination reaction of step (2) can be carried out either without any solvent, or by dissolving the diiodinated product in a suitable solvent (for instance a glycol such as diethylenglycol, or a long chain alcohol). To maximize the iodinated olefin yield, avoiding as far as possible a further dehydroiodination reaction with formation of the corresponding bis-olefin of formula CHR=CH-Z-CH=CHR, it is possible:

(a) to employ the base in defect with respect to the stoichiometric amount, with a molar ratio base/diiodinated compound preferably from 1.5 to 0.5, and then separating the iodinated olefin from the bis-olefin by fractional distillation; or

(b) to carry out the dehydroiodination reaction at reduced pressure, so as to remove the iodinated olefin from the reaction mixture as it forms, taking advantage of the fact that the latter has a boiling point lower than that of the starting diiodinated product; in such a case the reaction is preferably carried out without any solvent.

[0014] Alternatively, it is possible to carry out step (1) in defect of ethylene or propylene, to favour as much as possible formation of mono-addition product $I\text{-}Z\text{-}CH_2\text{-}CHR\text{-}I$ (which can be separated from the di-addition product by fractional distillation); the mono-addition product is then dehydroiodinated as described above, with formation of olefin I-Z-CH=CHR, which is finally submitted to a further addition of ethylene or propylene to give the iodinated olefin $I\text{-}CHRCH_2\text{-}Z\text{-}CH{=}CHR$.

[0015] When Z is a (per)fluoroalkylene radical, optionally containing one or more ether oxygen atoms, the starting diiodinated compound I-Z-I can be obtained by telomerization of a (per)fluoroolefin $C_2$-$C_4$ or of a (per)fluorovinylether $C_3$-$C_8$ (for instance tetrafluoroethylene, perfluoropropene, vinylidene fluoride, perfluoromethylvinylether, perfluoropropylvinylether, or mixtures thereof), by using a product of formula $I\text{-}(R_f)_k\text{-}I$ (where k = 0, 1; $R_f$ = $C_1$-$C_8$ (per)fluoroalkylene radical) as telogenic agent. Telomerization reactions of this type are described, for instance, by C. Tonelli and V. Tortelli in J. Fluorine Chem., 47 (1990), 199, or also in EP-200,908.

[0016] When Z is a (per)fluoropolyoxyalkylene radical, the preparation of the products I-Z-I is described, for instance, in US Patent 3,810,874.

[0017] The amount of monomeric units deriving from the iodinated olefin of formula (I) present in the fluoroelastomers object of the present invention is generally from 0.01 to 1.0 moles, preferably from 0.03 to 0.5 moles, even more preferably from 0.05 to 0.2 moles, per 100 moles of the other basic monomeric units.

[0018] The total iodine amount in the fluoroelastomers object of the present invention is, on the average, from 1.8 to 5.0, preferably from 2.0 to 4.0, iodine atoms per chain. The average number of iodine atoms per chain in terminal position is in turn generally from 1.0 to 2.0, preferably from 1.5 to 1.8. The iodine atoms in terminal position can be introduced, as described in US Patent 4,243,770, by adding during polymerization iodinated chain transfer agents, such as for instance compounds of formula $R_fI_x$, wherein $R_f$ is a (per)fluoroalkyl or a (per)fluorochloroalkyl having from 1 to 8 carbon atoms, while x is 1 or 2. In particular, the iodinated chain transfer agent can be selected from: 1,3-diiodoperfluoropropane, 1,4-diiodoperfluorobutane, 1,6-diiodoperfluorohexane, 1,3-diiodo-2-chloroperfluoropropane, 1,2-di(iododifluoromethyl)-perfluorocyclobutane, monoiodoperfluoroethane, monoiodoperfluorobutane, 2-iodo-1-hydroperfluoroethane, etc. Particualrly preferred are diiodinated chain transfer agents (x=2). Alternatively, it is possible to use as chain transfer agents alkali or alkaline-earth metal iodides, as described in US Patent 5,173,553. The amount of chain transfer agent to be added to the reaction medium is chosen according to the molecular weight which is intended to be obtained and to the chain transfer agent effectiveness.

[0019] The basic structure of the fluoroelastomers object of the present invention can be selected in particular from:

(1) VDF-based copolymers, where VDF is copolymerized with at least a comonomer selected from: perfluoroolefins $C_2$-$C_8$, such as tetrafluoroethylene (TFE), hexafluoropropene (HFP); $C_2$-$C_8$ chloro- and/or bromo-fluoroolefins, such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene; (per)fluoroalkylvinylethers (PAVE) $CF_2{=}CFOR_f$, wherein $R_f$ is a $C_1$-$C_6$ (per)fluoroalkyl, for instance trifluoromethyl, bromodifluoromethyl, pentafluoro-

propyl; (per)fluoro-oxyalkylvinylethers $CF_2$=CFXO, where X is a $C_1$-$C_{12}$ perfluoro-oxyalkyl having one or more ether groups, for instance perfluoro-2-propoxy-propyl; $C_2$-$C_8$ non-fluorinated olefins (Oℓ), for instance ethylene and propylene; typical compositions are the following: (a) VDF 45-85%, HFP 15-45%, TFE 0-30%; (b) VDF 50-80%, PAVE 5-50%, TFE 0-20%; (c) VDF 20-30%, Oℓ 10-30%, HFP and/or PAVE 18-27%, TFE 10-30%;

(2) TFE-based copolymers, where TFE is copolymerized with at least a comonomer selected from: (per)fluoroalkylvinylethers (PAVE) $CF_2$=$CFOR_f$, where $R_f$ is defined as above; (per)fluoro-oxyalkylvinylethers $CF_2$=CFOX, wherein X is defined as above; $C_2$-$C_8$ fluoroolefins containing hydrogen and/or chlorine and/or bromine atoms; $C_2$-$C_8$ non-fluorinated olefins (Oℓ); typical compositions are the following: (d) TFE 50-80%, PAVE 20-50%; (e) TFE 45-65%, Oℓ 20-55%, VDF 0-30%; (f) TFE 32-60%, Oℓ 10-40%, PAVE 20-40%; (g) TFE 33-75%, PAVE 15-45%, VDF 10-22%.

[0020] The preparation of the fluoroelastomers object of the present invention can be carried out by copolymerization of the monomers in aqueous emulsion according to methods well known in the art, in the presence of radical initiators (for instance alkali metal or ammonium persulphates, perphosphates, perborates or percarbonates), optionally in combination with ferrous, cuprous or silver salts or other easily oxidable metals. In the reaction medium are usually present also surfactants of various types, among which particularly preferred are the fluorinated surfactants of formula:

$$R_f\text{-}X^- M^+$$

wherein $R_f$ is a $C_5$-$C_{16}$ (per)fluoroalkyl chain or a (per)fluoropolyoxyalkylene chain, $X^-$ is $-COO^-$ or $-SO_3^-$, $M^+$ is selected from: $H^+$, $NH_4^+$, alkali metal ion. Among the most commonly used, we can cite: ammonium perfluorooctanoate, (per)fluoropolyoxyalkylenes terminated with one or more carboxyl groups, etc.

[0021] In a preferred embodiment, the fluoroelastomers object of the present invention are prepared in the presence of an aqueous microemulsion of perfluoropolyoxyalkylenes, as described in US Patent 4,864,006, or in the presence of an aqueous microemulsion of fluoropolyoxyalkylenes having hydrogenated end groups and/or hydrogenated repetitive units, as described in EP-625,526.

[0022] The amount of iodinated olefin of formula (I) to be added to the reaction mixture depends on the amount of units deriving therefrom which are intended to be obtained in the final product, bearing in mind that, at the low amounts employed according to the purposes of the present invention, practically the whole amount of the iodinated olefin present in the reaction medium enters the chain.

[0023] The polymerization reaction is generally carried out at a temperature of from 25° to 150°C, at a pressure up to 10 MPa.

[0024] When polymerization is completed, the fluoroelastomer is isolated from the emulsion by means of conventional methods, such as coagulation by addition of electrolytes or by cooling.

[0025] The peroxide curing is carried out, according to the art, by addition of a suitable peroxide capable of generating radicals by heating. Among the most commonly used we can cite: dialkylperoxides, such as for instance di-tertbutyl-peroxide and 2,5-dimethyl-2,5-di(tertbutylperoxy)hexane; dicumyl peroxide; dibenzoyl peroxide; ditertbutyl perbenzoate; di[1,3-dimethyl-3-(tertbutyl-peroxy)butyl]carbonate. Other peroxide systems are described, for instance, in EP Patents 136,596 and 410,351.

[0026] To the cure mixture other products are then added, such as:

(a) curing coagents, in an amount generally from 0.5 to 10%, preferably from 1 to 7%, by weight with respect to the polymer; among them commonly used are: triallyl-cyanurate; triallyl-isocyanurate (TAIC); tris (diallylamine)-s-triazine; triallylphosphite; N,N-diallylacrylamide; N,N,N',N'-tetraallyl-malonamide; trivinyl-isocyanurate; 2,4,6-trivinyl-methyltrisiloxane, etc.; TAIC is particularly preferred.

(b) a metal compound, in an amount of from 1 to 15%, preferably from 2 to 10%, by weight with respect to the polymer, selected from divalent metal oxides or hydroxides, such as for instance Mg, Zn, Ca or Pb, optionally associated to a weak acid salt, such as for instance Ba, Na, K, Pb, Ca stearates, benzoates, carbonates, oxalates, or phosphites;

(c) other conventional additives, such as fillers, pigments, antioxidants, stabilizers, and the like.

[0027] As said above, the fluoroelastomers object of the present invention do not require long post-curing treatments; to remove possible volatile by-products, after curing it is sufficient to treat the product in air for 30-60 minutes at 180°-230°C. As demonstrated by the experimentation carried out by the Applicant, longer post-curing periods do not lead to any significant improvement of mechanical and/or elastic properties of the product. This allows to drastically reduce processing times, with consequent increase of productivity for molding processes on an industrial scale.

[0028] The present invention will be now better illustrated by the following working examples, whose purpose is merely indicative but not limitative of the scope of the invention itself.

## EXAMPLE 1

Preparation of $CH_2=CH-(CF_2CF_2)_3-CH_2CH_2I$.

(1) Ethylene addition

[0029] In a 5 l AISI 316 steel reactor, equipped with a magnetic stirrer, previously evacuated and then brought to nitrogen atmosphere, were loaded: 1200 g (2.17 moles) of $I-(CF_2CF_2)_3-I$ (prepared as described in J. Fluorine Chemistry, 47 (1990). - 79); 12.4 g of CuI; 2.2 l of acetonitrile. The reactor was then pressurized with 5.0 moles of ethylene, and brought to a temperature of 160°C, and kept at such temperature for 10 hours under stirring. The pressure reached a maximum of 51 ate and then gradually decreased up to 10 ate. The reactor was then cooled down to room temperature, and the unreacted ethylene was discharged. The reaction mixture, containing sediments, was discharged and, after pre-stirring with excess of water, filtered on a buchner at reduced pressure, and washed with water. The collected solid was dried in an oven at 110°C. 1300 g of product were so obtained, which at gaschromatographic analysis showed a sole peak (yield: 98%). $^{19}$F-NMR and $^{1}$H-NMR analysis gave the following results:

$$(I-CH^e_2CH^d_2-CF^a_2CF^b_2CF^c_2)_2$$

$^{19}$F-NMR ($CDCl_3$) a = -114.5 ppm; b = -123 ppm; c = -121 ppm; a/b/c = 1/1/1

$^{1}$H-NMR e = 2.7 - 3.0 ppm; d = 3.4 ppm; e/d = 1/1.

(2) Dehydroiodination

[0030] In a 500 ml glass reactor, equipped with a mechanical stirrer, a thermometer, a dropping funnel with compensator, a water-cooled claisen with a gathering flask kept at -15°C (cold trap) were loaded: 80 g (0.131 moles) of $I-CH_2CH_2(CF_2CF_2)_3-CH_2CH_2I$ and 80 ml of diethylenglycol. The pressure in the system was reduced to 50 mmHg by means of a mechanical pump and the temperature brought to 130°C by immersion in an oil bath. A solution consisting of 15 g of NaOH dissolved in 50 ml of $H_2O$ was then gradually added (in about 30 min). Development of vapours, which condensed in the cold trap, revealed immediately that the reaction took place. At the end of the reaction, two phases were present in the cold trap, which were separated in a separating funnel. The aqueous phase was extracted with methylene chloride, which was then removed by distillation at reduced pressure. The so obtained organic phase and that left in the reactor were put together to give a total of 52.3 g of reaction products. By means of gaschromatography analysis, the mixture resulted to be formed by:

| | |
|---|---|
| $CH_2=CH-(CF_2CF_2)_3-CH=CH_2$ | 54% by weight |
| $I-CH_2CH_2-(CF_2CF_2)_3-CH=CH_2$ | 40% by weight |
| $I-CH_2CH_2-(CF_2CF_2)_3-CH_2CH_2-I$ | 6% by weight |

[0031] After fractional distillation, 20.3 g of iodinated olefin $I-CH_2CH_2-(CF_2CF_2)_3-CH=CH_2$ (purity: 99%; yield: 32%) were obtained.

Polymerization reaction

[0032] In a 5 l autoclave equipped with a stirrer working at 630 rpm, were charged, after evacuation, 3.5 l of demineralized water and 36 ml of a microemulsion obtained by mixing:

- 7.8 ml of an acid terminated perfluoropolyoxyalkylene of formula:

$$CF_3O(CF_2-CF(CF_3)O)_n(CF_2O)_mCF_2COOH$$

where n/m = 10, having average molecular weight of 600;
- 8.9 ml of a 30% by volume $NH_4OH$ aqueous solution;
- 15.6 ml of demineralized water;
- 4.8 ml of Galden$^{(R)}$ D02 of formula:

$$CF_3O(CF_2\text{-}CF(CF_3)O)_n(CF_2O)_mCF_3$$

wherein n/m = 20, having average molecular weight of 450.

[0033] The autoclave was then brought to 80°C and kept at such temperature for the whole duration of the reaction. The following mixture of monomers was then fed:

| | |
|---|---|
| VDF | 24.0% by moles |
| HFP | 59.5% by moles |
| TFE | 16.5% by moles |

[0034] so as to bring the pressure to 25 bar.
[0035] In the autoclave were then introduced:

- 112 ml of an aqueous solution of ammonium persulphate (APS) having a concentration of 1 g/l;
- 1,6-diiodoperfluorohexane ($C_6F_{12}I_2$) as chain transfer agent, in the form of a solution obtained dissolving 6.0 ml of the iodinated product in 14.0 ml of the same Galden(R) D02 used for the microemulsion; the addition was carried out in 20 portions, each portion of 1.0 ml, at the polymerization start and for each 5% increase in the monomer conversion;
- the iodinated olefin of formula $CH_2{=}CH\text{-}(CF_2CF_2)^3\text{-}CH_2CH_2I$, in the form of a solution obtained dissolving 3.0 ml in 47.0 ml of the same Galden(R) D02 described above; the addition was carried out in 20 portions, each portion of 2.5 ml, at the polymerization start and for each 5% increase in the monomer conversion.

[0036] The pressure of 25 bar was kept constant for the whole duration of the polymerization by feeding a mixture consisting of:

| | |
|---|---|
| VDF | 50% by moles |
| HFP | 26% by moles |
| TFE | 24% by moles. |

[0037] After 300 minutes of reaction, the autoclave was cooled, the latex drained and the polymer coagulated by addition of an aluminum sulphate solution (6 g of sulphate per liter of latex). After washing, the so obtained product was dried in an oven for 24 hours at 70°C. 1500 g of product were so obtained, which was characterized as reported in Table 1. The polymer monomer composition was determined by $^{19}F$-NMR analysis, the iodine percentage by X-ray fluorescence measurements. The osmometric average molecular weight ($M_n^{osm}$) was calculated, by calibration curves, from molecular weight values measured by Gel Permeation Chromatography (GPC).
[0038] The polymer was then peroxide cured: the vulcanization mixture composition and the characteristics of the cured product are reported in Table 2. It is to be noticed that, differently from the products of the prior art, a prolonged post-curing treatment (24 hours at 200°C) did not lead to any improvement of mechanical and elastic properties of the cured product if compared with a shorter treatment (only 1 hour at 200°C).

## EXAMPLE 2

[0039] Example 1 was repeated, except that during the polymerization step 6 ml of the same iodinated olefin, dissolved in 94 ml of the same Galden(R) D02 were introduced in the reactor. The addition was carried out in 20 portions of 5 ml, at the reaction start and each 5% increase in the monomer conversion. The reaction was discontinued by cooling after 303 minutes, obtaining 1300 g of polymer. The characteristics of the product as such and after peroxide curing are reported in Tables 1 and 2, respectively.

EXAMPLE 3 (comparative)

[0040] Following the same procedure as described in Example 1, a polymer of the same type but without the iodinated olefin was prepared. The properties of the product as such and after peroxide curing are reported in Tables 1 and 2, respectively.

TABLE 1

| EXAMPLE | | 1 | 2 | 3(*) |
|---|---|---|---|---|
| Polymer composition (%mole) | | | | |
| VDF | | 53.9 | 55.6 | 54.0 |
| HFP | | 20.3 | 19.9 | 21.5 |
| TFE | | 25.9 | 24.5 | 24.5 |
| iodinated olefin | | 0.06 | 0.13 | -- |
| Total iodine | (% weight) | 0.29 | 0.41 | 0.22 |
| | (per chain) | 1.83 | 2.23 | 1.38 |
| Mooney Viscosity (ASTM D1646) ML(1+10') 121°C | | 46 | 32 | 45 |
| $M_n^{osm}$ | | 80,000 | 69,000 | 80,000 |
| $T_g$ onset (°C) (DSC - ASTM D3418-82) | | -13.4 | -13.5 | -12.0 |

(*) comparative

TABLE 2

| EXAMPLE | 1 | 2 | 3(*) |
|---|---|---|---|
| Vulcanization mixture composition | | | |
| Polymer (g) | 100 | 100 | 100 |
| Luperco(R) 101 XL (phr) | 3 | 3 | 3 |
| Drimix(R) TAIC ( " ) | 4 | 4 | 4 |
| ZnO ( " ) | 5 | 5 | 5 |
| Carbon black MT ( " ) | 30 | 30 | 30 |
| Vulcanization mixture characteristics | | | |
| *Mooney Viscosity ML(1+10')$^{121°C}$ (ASTM D1646) | 45 | 33 | 41 |
| *ODR 177°C arc 3, 12' (ASTM D2084-81) | | | |
| ML (N·m) | 1.23 | 0.78 | 1.12 |
| MH ( " ) | 15.8 | 16.8 | 13.9 |
| $t_{s2}$ (sec) | 51 | 51 | 57 |
| $t_{s50}$ ( " ) | 81 | 81 | 93 |
| $t'_{90}$ ( " ) | 117 | 114 | 115 |
| $V_{max}$ (N·m/sec) | 0.30 | 0.35 | 0.30 |
| Characteristics after curing in press at 170°C for 10' (ASTM D412-83) | | | |
| Modulus at 100% (MPa) | 4.8 | 4.5 | 3.6 |
| Stress at break (MPa) | 17.3 | 16.7 | 17.2 |
| Elongation at break (%) | 226 | 215 | 295 |
| Shore A hardness (points) | 69 | 71 | 72 |
| Characteristics after post-curing in oven at 200°C for 1 hour | | | |
| *MECHANICAL PROPERTIES (ASTM D412-83) | | | |
| Modulus at 100% (MPa) | 6.5 | 6.8 | 4.9 |
| Stress at break (MPa) | 21.2 | 20.4 | 20.7 |
| Elongation at break (%) | 205 | 196 | 273 |
| Shore A hardness (points) | 72 | 74 | 72 |
| *COMPRESSION SET (at 200°C for 70 hours - ASTM D395 Method B) | | | |
| O-ring 214 (%) | 19 | 18 | 27 |
| Characteristics after post-curing in oven at 200°C for 24 hours | | | |
| *MECHANICAL PROPERTIES (ASTM D412-83) | | | |
| Modulus at 100% (MPa) | 6.8 | 7.3 | 4.7 |
| Stress at break (MPa) | 21.1 | 20.0 | 19.2 |
| Elongation at break (%) | 198 | 192 | 272 |
| Shore A hardness (points) | 72 | 74 | 72 |
| *COMPRESSION SET (at 200°C for 70 hours - ASTM D395 Method B) | | | |
| O-ring 214 (%) | 18 | 18 | 30 |

(*) comparative

## EXAMPLE 4

[0041] In a 10 l autoclave, equipped with a stirrer working at 545 rpm, were loaded, after evacuation, 6.7 l of demineralized water and 66.9 ml of a microemulsion obtained by mixing:

- 14.5 ml of an acid terminated perfluoropolyoxyalkylene of formula:

$$CF_3O(CF_2\text{-}CF(CF_3)O)_n(CF_2O)_mCF_2COOH$$

wherein n/m = 10, having average molecular weight of 600;
- 14.5 ml of a 30% by volume $NH_4OH$ aqueous solution;
- 29.0 ml of demineralized water;
- 8.9 ml of Galden(R) D02 of formula:

$$CF_3O(CF_2\text{-}CF(CF_3)O)_n(CF_2O)_mCF_3$$

wherein n/m = 20, having average molecular weight of 450.

[0042] The autoclave was then brought to 80°C and kept at such temperature for the whole duration of the reaction. The following monomer mixture was then fed:

| | |
|---|---|
| VDF | 64.5% by moles |
| MVE | 32.0% by moles |
| TFE | 3.5% by moles |
| (MVE = perfluoromethylvinylether) | |

so as to bring the pressure to 25 bar.

[0043] In the autoclave were then introduced:

- 214 ml of a ammonium persulphate aqueous solution (APS) having concentration of 1 g/l;
- 1,6-diiodoperfluorohexane ($C_6F_{12}I_2$) as chain transfer agent, in the form of a solution obtained by dissolving 7.6 ml of the iodinated product in 12.4 ml of the same Galden(R) D02 used for the microemulsion;
- the iodinated olefin of formula $CH_2{=}CH\text{-}(CF_2CF_2)_3\text{-}CH_2CH_2I$, in the form of a solution obtained by dissolving 5.0 ml in 95.0 ml of the same Galden(R) D02 described above; the addition was carried out in 20 portions, each portion of 5 ml, at the polymerization start and each 5% increase in monomer conversion.

[0044] The pressure of 25 bar was kept constant for the whole duration of the polymerization by feeding a mixture consisting of:

| | |
|---|---|
| VDF | 75% by moles |
| MVE | 21% by moles |
| TFE | 4% by moles. |

[0045] After 187 minutes of reaction, the autoclave was cooled, the latex drained and the polymer coagulated by addition of an aluminum sulphate solution (6 g of sulphate per liter of latex). After washing, the so obtained product was dried in an oven for 24 hours at 70°C. 2500 g of product were so obtained, which was characterized as reported in Table 3.

[0046] The polymer was then peroxide cured: the vulcanization mixture composition and the characteristics of the cured product are reported in Table 4.

**EXAMPLE 5** (comparative)

[0047] Following the same procedure as described in Example 4, a polymer of the same type but without the iodinated olefin was prepared. The properties of the product as such and after peroxide curing are reported in Tables 3 and 4

respectively.

TABLE 3

| EXAMPLE | | 4 | 5(*) |
|---|---|---|---|
| Polymer composition (%mole) | | | |
| VDF | | 79.0 | 80.2 |
| HFP | | 17.0 | 15.7 |
| TFE | | 4.0 | 4.0 |
| iodinated olefin | | 0.05 | -- |
| Total iodine | (% peso) | 0.30 | 0.26 |
| | (per chain) | 1.53 | 1.31 |
| Mooney viscosity (ASTM D1646) | | | |
| ML(1+10') 121°C | | 28 | 28 |
| ML(1+4') 100°C | | 52 | 58 |
| $M_n^{osm}$ | | 65,000 | 64,000 |
| $T_g$ onset (°C) (DSC - ASTM D3418-82) | | -36.1 | -37.0 |

(*) comparative

TABLE 4

| EXAMPLE | 4 | 5(*) |
|---|---|---|
| **Vulcanization mixture composition** | | |
| Polymer (g) | 100 | 100 |
| Luperco(R) 101 XL (phr) | 3 | 3 |
| Drimix(R) TAIC ( " ) | 4 | 4 |
| ZnO ( " ) | 5 | 5 |
| Carbon black MT ( " ) | 30 | 30 |
| **Vulcanization mixture characteristics** | | |
| *Mooney Viscosity ML(1+10')$^{121°C}$ (ASTM D1646) | 30 | 33 |
| *ODR 177°C arc 3, 12' (ASTM D2084-81) | | |
| ML (N·m) | 0.78 | 0.78 |
| MH ( " ) | 15.04 | 12.65 |
| $t_{s2}$ (sec) | 51 | 57 |
| $t_{s50}$ ( " ) | 81 | 87 |
| $t'_{90}$ ( " ) | 111 | 114 |
| $V_{max}$ (N·m/sec) | 0.37 | 0.32 |
| **Characteristics after curing in press at 170°C for 10'** (ASTM D412-83) | | |
| Modulus at 100% (MPa) | 3.4 | 2.6 |
| Stress at break (MPa) | 14.5 | 13.5 |
| Elongation at break (%) | 236 | 324 |
| Shore A hardness (points) | 66 | 64 |
| **Characteristics after post-curing in oven at 200°C for 1 hour** | | |
| *MECHANICAL PROPERTIES (ASTM D412-83) | | |
| Modulus at 100% (MPa) | 3.6 | 2.9 |
| Stress at break (MPa) | 16.3 | 15.5 |
| Elongation at break (%) | 237 | 292 |
| Shore A hardness (points) | 67 | 66 |
| *COMPRESSION SET | | |
| (at 200°C for 70 hours - ASTM D395 Method B) | | |
| O-ring 214 (%) | 24 | 36 |
| **Characteristics after post-curing in oven at 200°C for 24 hours** | | |
| *MECHANICAL PROPERTIES (ASTM D412-83) | | |
| Modulus at 100% (MPa) | 6.8 | 4.7 |
| Stress at break (MPa) | 21.1 | 19.2 |
| Elongation at break (%) | 198 | 272 |
| Shore A hardness (points) | 72 | 72 |
| *COMPRESSION SET | | |
| (at 200°C for 70 hours - ASTM D395 Method B) | | |
| O-ring 214 (%) | 22 | 33 |

(*) comparative

## Claims

1. Peroxide curable fluoroelastomers, having iodine atoms in terminal position, and monomeric units in the chain deriving from an iodinated olefin of formula:

$$CHR{=}CH\text{-}Z\text{-}CH_2CHR\text{-}I \qquad (I)$$

wherein: R is -H or $-CH_3$; Z is a $C_1$-$C_{18}$ (per) fluoroalkylene radical, linear or branched, optionally containing one or more ether oxygen atoms, or a (per)fluoropolyoxyalkylene radical.

2. Fluoroelastomers according to claim 1, wherein in formula (I) Z is a $C_4$-$C_{12}$ perfluoroalkylene radical.

3. Fluoroelastomers according to claim 1, wherein in formula (I) Z is a (per)fluoropolyoxyalkylene radical of formula:

$$-(Q)_p\text{-}CF_2O\text{-}(CF_2CF_2O)_m(CF_2O)_n\text{-}CF_2\text{-}(Q)_p\text{-} \qquad (II)$$

wherein: Q is a $C_1$-$C_6$ alkylene or oxyalkylene radical; p is 0 or 1; m and n are numbers such that the ratio m/n is from 0.2 to 5 and the molecular weight of said (per)fluoropolyoxyalkylene radical is from 400 to 10,000.

4. Fluoroelastomers according to claim 3, wherein Q is selected from: $-CH_2O-$; $-CH_2OCH_2-$; $-CH_2-$; $-CH_2CH_2-$.

5. Fluoroelastomers according to anyone of the previous claims, wherein the amount of units deriving from the iodinated olefin of formula (I) is from 0.01 to 1.0% by mole per 100 moles of the other basic monomeric units.

6. Fluoroelastomers according to claim 5, wherein the amount of units deriving from the iodinated olefin of formula (I) is from 0.03 to 0.5% by mole per 100 moles of the other basic monomeric units.

7. Fluoroelastomers according to anyone of the previous claims, wherein the average number of iodine atoms per chain in terminal position is from 1.0 to 2.0.

8. Fluoroelastomers according to claim 7, wherein the average number of iodine atoms per chain in terminal position is from 1.5 to 1.8.

9. Fluoroelastomers according to anyone of the previous claims, wherein the total amount of iodine atoms per chain is, on the average, from 1.8 to 5.0.

10. Fluoroelastomers according to any of the previous claims, wherein the total amount of iodine atoms per chain is, on the average, from 2.0 to 4.0.

11. Fluoroelastomers according to claim 1, wherein the monomeric structure is based on vinylidene fluoride (VDF), copolymerized with at least a comonomer selected from: $C_2$-$C_8$ perfluoroolefins; chloro- and/or bromofluoroolefins $C_2$-$C_8$; (per)fluoroalkylvinylethers (PAVE) $CF_2{=}CFOR_f$, where $R_f$ is a $C_1$-$C_6$ (per)fluoroalkyl; (per)fluoro-oxyalkylvinylethers $CF_2{=}CFOX$, where X is a $C_1$-$C_{12}$ (per)fluoro-oxyalkyl having one or more ether groups; $C_2$-$C_8$ non-fluorinated olefins ($O\ell$).

12. Fluoroelastomers according to claim 11, wherein the basic monomeric structure is selected from: (a) VDF 45-85%, HFP 15-45%, TFE 0-30%; (b) VDF 50-80%, PAVE 5-50%, TFE 0-20%; (c) VDF 20-30%, $O\ell$ 10-30%, HFP and/or PAVE 18-27%, TFE 10-30%.

13. Fluoroelastomers according to claim 1, wherein the monomeric structure is based on tetrafluoroethylene (TFE), copolymerized with at least a comonomer selected from: (per)fluoroalkylvinylethers (PAVE) $CF_2{=}CFOR_f$, where $R_f$ is a $C_1$-$C_6$ (per)fluoroalkyl; perfluorooxyalkylvinylethers $CF_2{=}CFOX$, where X is a $C_1$-$C_{12}$ (per)fluorooxyalkyl having one or more ether groups; $C_2$-$C_8$ fluoroolefins containing hydrogen and/or chlorine and/or bromine atoms; $C_2$-$C_8$ non-fluorinated olefins ($O\ell$).

14. Fluoroelastomers according to claim 13, wherein the basic monomeric structure is selected from: (d) TFE 50-80%, PAVE 20-50%; (e) TFE 45-65%, $O\ell$ 20-55%, VDF 0-30%; (f) TFE 32-60%, $O\ell$ 10-40%, PAVE 20-40%; (g) TFE 33-75%, PAVE 15-45%, VDF 10-22%.

15. Fluoroelastomers according to anyone of the previous claims, obtainable by a copolymerization process of the monomers in aqueous emulsion in the presence of a radical initiator and of an iodinated chain transfer agent.

16. Fluoroelastomers according to claim 15, wherein the iodinated chain transfer agent is a compound of formula $R_fI_x$,

wherein $R_f$ is a (per)fluoroalkyl or a (per)fluorochloroalkyl having from 1 to 8 carbon atoms, while x is 1 or 2.

17. Fluoroelastomers according to claim 15 or 16, wherein the copolymerization process of the monomers is carried out in the presence of an aqueous microemulsion of perfluoropolyoxyalkylenes or of fluoropolyoxyalkylenes having hydrogenated end groups and/or hydrogenated repetitive units.

18. Iodinated olefins of formula (I), defined according to claims from 1 to 4.

19. Process for preparing the iodinated olefins of claim 18, which comprises in sequence:

(1) adding ethylene or propylene to a compound of formula I-Z-I, to obtain a diiodinated product having the formula:

$$\text{I-CHR-CH}_2\text{-Z-CH}_2\text{-CHR-I} \qquad \text{(III)}$$

wherein R and Z are defined as above;
(2) partially dehydroiodinating the product of formula (III) with a base so as to obtain the iodinated olefin of formula (I).

20. Process according to claim 19, wherein step (2) is carried out in defect of the base, and afterwards the iodinated olefin is separated by fractional distillation.

21. Process according to claim 19, wherein the step (2) is carried out at reduced pressure, so as to remove the iodinated olefin from the reaction mixture as it forms.

22. Process according to claim 19, wherein step (1) is carried out in defect of ethylene or propylene, so as to favour formation of mono-addition product I-Z-$CH_2$-CHR-I; the mono-addition product is then dehydroiodinated according to step (2), with formation of the olefin I-Z-CH=CHR, which is finally subjected to futher addition of ethylene or propylene to give the iodinated olefin of formula (I).

23. Use of the fluoroelastomers according to claims from 1 to 16 for manufacturing O-rings.

24. Use according to claim 23, wherein the fluoroelastomers have basic monomeric composition according to claim 14.

## Patentansprüche

1. Peroxidhärtbare Fluorelastomere mit Iodatomen in endständiger Position und Monomereinheiten in der Kette, die von einem iodierten Olefin der Formel

$$\text{CHR=CH-Z-CH}_2\text{CHR-I} \qquad \text{(I)}$$

stammen, wobei R gleich -H oder -$CH_3$ ist; Z ein $C_1$-$C_{18}$-(Per)fluoralkylenrest, linear oder verzweigt, der gegebenenfalls ein oder mehrere Ether-Sauerstoffatome enthält, oder ein (Per)fluorpolyoxyalkylenrest ist.

2. Fluorelastomere nach Anspruch 1, wobei in Formel (I) Z ein $C_4$-$C_{12}$-Perfluoralkylenrest ist.

3. Fluorelastomere nach Anspruch 1, wobei in Formel (I) Z ein (Per)fluorpolyoxyalkylenrest der Formel

$$\text{-(Q)}_p\text{-CF}_2\text{O-(CF}_2\text{CF}_2\text{O)}_m\text{(CF}_2\text{O)}_n\text{-CF}_2\text{-(Q)}_p\text{-} \qquad \text{(II)}$$

ist, wobei Q ein $C_1$-$C_6$-Alkylen- oder -Oxyalkylenrest ist; p gleich 0 oder 1 ist; m und n ganze Zahlen sind, so daß das Verhältnis m/n von 0,2 bis 5 reicht und das Molekulargewicht des (Per)fluorpolyoxyalkylenrests von 400 bis 10 000 reicht.

4. Fluorelastomere nach Anspruch 3, wobei Q ausgewählt ist aus: -$CH_2$O-; -$CH_2$O$CH_2$-; -$CH_2$-; -$CH_2CH_2$-.

5. Fluorelastomere nach einem der vorherigen Ansprüche, wobei die Menge an von dem iodierten Olefin der Formel (I) abstammenden Einheiten von 0,01 bis 1,0 Mol-% pro 100 Mol der anderen monomeren Grundeinheiten beträgt.

6. Fluorelastomere nach Anspruch 5, wobei die Menge an von dem iodierten Olefin der Formel (I) abstammenden Einheiten von 0,03 bis 0,5 Mol-% pro 100 Mol der anderen monomeren Grundeinheiten beträgt.

7. Fluorelastomere nach einem der vorherigen Ansprüche, wobei die mittlere Zahl an Iodatomen pro Kette in endständiger Position von 1,0 bis 2,0 reicht.

8. Fluorelastomere nach Anspruch 7, wobei die mittlere Zahl an Iodatomen pro Kette in endständiger Position von 1,5 bis 1,8 reicht.

9. Fluorelastomere nach einem der vorherigen Ansprüche, wobei die Gesamtmenge an Iodatomen pro Kette im Mittel von 1,8 bis 5,0 reicht.

10. Fluorelastomere nach einem der vorherigen Ansprüche, wobei die Gesamtmenge an Iodatomen pro Kette im Mittel von 2,0 bis 4,0 reicht.

11. Fluorelastomere nach Anspruch 1, wobei die Monomerstruktur auf Vinylidenfluorid (VDF) basiert, das mit mindestens einem Comonomer copolymerisiert ist, ausgewählt aus: $C_2$-$C_8$-Perfluorolefinen; $C_2$-$C_8$-Chlor- und/oder -Bromfluorolefinen; (Per)fluoralkylvinylethern (PAVE) $CF_2=CFOR_f$, wobei $R_f$ ein $C_1$-$C_6$-(Per)fluoralkyl ist; Perfluoroxyalkylvinylethern $CF_2=CFOX$, wobei X ein $C_1$-$C_{12}$-Perfluoroxyalkyl mit einer oder mehreren Ethergruppen ist; nichtfluorierten $C_2$-$C_8$-Olefinen (Ol).

12. Fluorelastomere nach Anspruch 11, wobei die Monomergrundstruktur ausgewählt ist aus:

    (a) VDF 45-85%, HFP 15-45%, TFE 0-30%;
    (b) VDF 50-80%, PAVE 5-50%, TFE 0-20%;
    (c) VDF 20-30%, Ol 10-30%, HFP und/oder PAVE 18-27%, TFE 10-30%.

13. Fluorelastomere nach Anspruch 1, wobei die Monomerstruktur auf Tetrafluorethylen (TFE) basiert, das mit mindestens einem Comonomer copolymerisiert ist, ausgewählt aus: (Per)fluoralkylvinylethern (PAVE) $CF_2=CFOR_f$, wobei $R_f$ ein $C_1$-$C_6$-(Per)fluoralkyl ist; Perfluoroxyalkylvinylethern $CF_2=CFOX$, wobei X ein $C_1$-$C_{12}$-Perfluoroxyalkyl mit einer oder mehreren Ethergruppen ist; $C_2$-$C_8$-Fluorolefinen, die Wasserstoff- und/oder Chlor- und/oder Bromatome enthalten; nichtfluorierten $C_2$-$C_8$-Olefinen (Ol).

14. Fluorelastomere nach Anspruch 13, wobei die Monomergrundstruktur ausgewählt ist aus:

    (d) TFE 50-80%, PAVE 20-50%;
    (e) TFE 45-65%, Ol 20-55%, VDF 0-30%;
    (f) TFE 32-60%, Ol 10-40%, PAVE 20-40%;
    (g) TFE 33-75%, PAVE 15-45%, VDF 10-22%.

15. Fluorelastomere nach einem der vorherigen Ansprüche, die erhältlich sind durch ein Copolymerisationsverfahren der Monomeren in einer wäßrigen Emulsion in Gegenwart eines Radikalstarters und eines iodierten Kettenübertragungsreagens.

16. Fluorelastomere nach Anspruch 15, wobei das iodierte Kettenübertragungsreagens eine Verbindung der Formel $R_fI_x$ ist, wobei $R_f$ ein (Per)fluoralkyl oder ein (Per)fluorchloralkyl mit von 1 bis 8 Kohlenstoffatomen ist, während x gleich 1 oder 2 ist.

17. Fluorelastomere nach Anspruch 15 oder 16, wobei das Copolymerisationsverfahren der Monomere durchgeführt wird in Gegenwart einer wäßrigen Mikroemulsion von Perfluorpolyoxyalkylenen oder von Fluorpolyoxyalkylenen mit hydrierten Endgruppen und/oder hydrierten Repetiereinheiten.

18. Iodierte Olefine der Formel (I), die gemäß der Ansprüche 1 bis 4 definiert sind.

19. Verfahren zur Herstellung der iodierten Olefine gemäß Anspruch 18, umfassend der Reihe nach:

    (1) Zugeben von Ethylen oder Propylen zu einer Verbindung der Formel I-Z-I, um ein diiodiertes Produkt mit der Formel

$$I\text{-}CHR\text{-}CH_2\text{-}Z\text{-}CH_2\text{-}CHR\text{-}I \quad (III)$$

zu erhalten, wobei R und Z wie oben definiert sind;

(2) partielles Dehydroiodieren des Produkts der Formel (III) mit einer Base, so daß das iodierte Olefin der Formel (I) erhalten wird.

20. Verfahren nach Anspruch 19, wobei der Schritt (2) bei einem Unterschuß an Base durchgeführt wird und anschließend das iodierte Olefin durch fraktionierte Destillation abgetrennt wird.

21. Verfahren nach Anspruch 19, wobei der Schritt (2) bei reduziertem Druck durchgeführt wird, so daß das iodierte Olefin bei seiner Bildung aus der Reaktionsmischung entfernt wird.

22. Verfahren nach Anspruch 19, wobei der Schritt (1) bei einem Unterschuß an Ethylen oder Propylen durchgeführt wird, so daß die Bildung eines Monoadditionsprodukts $I\text{-}Z\text{-}CH_2\text{-}CHR\text{-}I$ begünstigt wird; das Monoadditionsprodukt dann gemäß Schritt (2) dehydroiodiert wird, unter Bildung des Olefins $I\text{-}Z\text{-}CH{=}CHR$, welches schließlich einer weiteren Addition von Ethylen oder Propylen unterzogen wird, um das iodierte Olefin der Formel (I) zu ergeben.

23. Verwendung der Fluorelastomere gemäß den Ansprüchen 1 bis 16 zur Herstellung von O-Ringen.

24. Verwendung nach Anspruch 23, wobei die Fluorelastomere eine Monomergrundzusammensetzung gemäß Anspruch 14 besitzen.

## Revendications

1. Fluoroélastomères vulcanisables au peroxyde, ayant des atomes d'iode en position terminale et des motifs monomères dans la chaîne dérivant d'une oléfine iodée de formule :

$$CHR{=}CH\text{-}Z\text{-}CH_2CHR\text{-}I \quad (I)$$

dans laquelle : R est -H ou $CH_3$ ; Z est un radical (per)fluoroalkylène en $C_1$ à $C_{18}$ linéaire ou ramifié, renfermant éventuellement un ou plusieurs atomes d'oxygène éther, ou un radical (per)fluoropolyoxyalkylène.

2. Fluoroélastomères selon la revendication 1, dans lesquels, dans la formule (I), Z est un radical (per)fluoroalkylène en $C_4$ à $C_{12}$.

3. Fluoroélastomères selon la revendication 1, dans lesquels, dans la formule (I), Z est un radical (per)fluoropolyoxyalkylène de formule :

$$-(Q)_p\text{-}CF_2O\text{-}(CF_2CF_2O)_m(CF_2O)_n\text{-}CF_2\text{-}(Q)_p\text{-} \quad (II)$$

dans laquelle : Q est un radical alkylène ou oxyalkylène en $C_1$ à $C_6$ ; p est égal à 0 ou 1 ; m et n sont des nombres tels que le rapport m/n soit compris entre 0,2 et 5 et la masse moléculaire dudit radical perfluoropolyoxyalkylène soit comprise entre 400 et 10 000.

4. Fluoroélastomères selon la revendication 3, dans lesquels Q est choisi parmi $-CH_2O-$, $-CH_2OCH_2-$ ; $-CH_2-$ ; $-CH_2CH_2-$.

5. Fluoroélastomères selon l'une quelconque des revendications précédentes, dans lesquels la quantité de motifs dérivant de l'oléfine iodée de formule (I) représente 0,01 à 1,0 % en mole pour 100 moles d'autres motifs monomères de base.

6. Fluoroélastomères selon la revendication 5, dans lesquels la proportion de motifs dérivant de l'oléfine iodée de formule (I) représente de 0,03 à 0,5% en mole pour 100 moles des autres motifs monomères de base.

7. Fluoroélastomères selon l'une quelconque des revendications précédentes, dans lesquels le nombre moyen d'atomes d'iode par chaîne en position terminale est de 1,0 à 2,0.

8. Fluoroélastomères selon la revendication 7, dans lesquels le nombre moyen d'atomes d'iode par chaîne en position terminale est compris entre 1,5 et 1,8.

9. Fluoroélastomères selon l'une quelconque des revendications précédentes, dans lesquels la quantité totale d'atomes d'iode par chaîne est en moyenne de 1,8 à 5,0.

10. Fluoroélastomères selon l'une quelconque des revendications précédentes, dans lesquels la quantité totale d'atomes d'iode par chaîne est, en moyenne de 2,0 à 4,0.

11. Fluoroélastomères selon la revendication 1, dans lesquels la structure monomère est basée sur du fluorure de vinylidène (VDF) copolymérise avec au moins un monomère choisi parmi : perfluoro-oléfines en $C_2$ a $C_8$ ; chloro- et/ou bromofluoro-oléfines en $C_2$ à $C_8$ ; (per)-fluoroalkylvinyléthers (PAVE) $CF_2$=$CFOR_f$, où $R_f$ est un (per)fluoroalkyle en $C_1$ à $C_6$;(per)fluoro-oxyalkylvinyléthers $CH_2$=CFOX, ou X est un (per)fluoro-oxyalkyle en $C_1$ à $C_{12}$ comportant un ou plusieurs groupes éthers ; une oléfine en $C_2$ à $C_8$ non fluorée (Ol).

12. Fluoroélastomères selon la revendication 11, dans lesquels la structure monomère de base est choisie parmi (a) VDF 45-85 %, HFP 15-45 %, TFE 0-30 % ; (b) VDF 50-80 %, PAVE 5-50 %, TFE 0-20 % ; (c) VDF 20-30 %, Ol 10-30 %, HFP et/ou PAVE 18-27 %, TFE 10-30 %.

13. Fluoroélastomères selon la revendication 1, dans lesquels la structure monomère est à base de tétrafluoroéthylène (TFE) copolymérisé avec au moins un comonomère choisi parmi : (per)fluoroalkylvinyléthers (PAVE) $CF_2$=$CFOR_f$, où $R_f$ est un (per)fluoroalkyle en $C_1$ à $C_6$ ; perfluoro-oxyalkylvinyléthers $CF_2$=CFOX, où X est un (per)fluoro-oxyalkyle en $C_1$ à $C_{12}$ comportant un ou plusieurs groupes éther ; fluoro-oléfines en $C_2$ à $C_8$ contenant des atomes d'hydrogène et/ou de chlore et/ou de brome; oléfines non fluorées en $C_2$ à $C_8$ (Ol).

14. Fluoroélastomères selon la revendication 13, dans lesquels la structure monomère de base est choisie parmi ; (d) TFE 50-80 %, PAVE 20-50 % ; (e) TFE 45-65 %, Ol 20-55 %, VDF 0-30 % ; (f) TFE 32-60 %, Ol 10-40 %, PAVE 20-40 % ; (g) TFE 33-75 %, PAVE 15-45 %, VDF 10-20 %.

15. Fluoroélastomères selon l'une quelconque des revendications précédentes, pouvant être obtenus par un procédé de copolymérisation de monomères en émulsion aqueuse en présence d'un initiateur radicalaire et d'un agent de transfert de chaîne iodé.

16. Fluoroélastomères selon la revendication 15, dans lesquels l'agent de transfert de chaîne iode est un compose de formule $R_fI_x$, ou $R_f$ est un (per) fluoroalkyle ou un (per)fluorochloroalkyle comportant de 1 à 8 atomes de carbone, tandis que x vaut 1 ou 2.

17. Fluoroélastomères selon la revendication 15 ou 16, dans lesquels le procédé de copolymérisation des monomères est mis en oeuvre en présence d'une microémulsion aqueuse de perfluoropolyoxyalkylènes ou de fluoropolyoxyalkylènes comportant des groupes terminaux hydrogénés et/ou des motifs répétitifs hydrogénés

18. Oléfines iodées de formule (I) définies selon l'une quelconque des revendications 1 à 4.

19. Procédé de préparation d'oléfines iodées selon la revendication 18, qui comprend successivement :

(1) l'addition de l'éthylène ou du propylène a un composé de formule I-Z-I pour obtenir un produit diiode repondant à la formule :

$$\text{I-CHR-CH}_2\text{-Z-CH}_2\text{-CHR-I} \qquad \text{(III)}$$

dans laquelle R et Z sont tels que définis ci-dessus ;
(2) deshydroiodation partielles du produit de formule (III) à l'aide d'une base de façon à obtenir l'oléfine iodé de formule (I).

20. Procédé selon la revendication 19, dans lequel on effectue l'étape (2) en présence d'un défaut de base et ensuite, on sépare l'oléfine iodée par distillation fractionnée.

21. Procédé selon la revendication 19, dans lequel on effectue l'étape (2) sous pression réduite de façon a eliminer

l'oléfine iodée du mélange réactionnel au fur et à mesure de sa formation.

22. Procédé selon la revendication 19, dans lequel on effectue l'étape (1) en présence d'un défaut d'éthyléne ou de propylène de façon à favoriser la formation de produits de mono-addition I-Z-$CH_2$-CHR-I ; on soumet le produit de mono-addition à une déshydro-iodation selon la revendication 2 avec formation de l'oléfine I-Z-CH=CHR, qu'on soumet finalement à une addition supplémentaire d'éthylène ou de propylène pour obtenir l'oléfine iodée de formule (I).

23. Utilisation des fluoroélastomères selon les revendications 1 à 16, pour la fabrication de joints toriques.

24. Utilisation selon la revendication 23, dans laquelle les fluoroélastomères ont des compositions en monomères de base selon la revendication 14.